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Metastable surface phase for Na_xC_{60}

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Abstract

Na_xC_{60} thin films with Na concentration $0 \leqslant x \leqslant 3$ were investigated using angle-dependent photoelectron spectroscopy. For low doping we observed two distinct fulleride phases coexisting with regions of pristine C_{60}. One of these fulleride phase is predominantly formed close to the surface and disappears after annealing and further addition of Na. At higher doping a phase with stoichiometry of $x = 3$ is formed.

Keywords: Fullerenes; Photoelectron spectroscopy

1. Introduction

Alkali metal fullerides (A_xC_{60}) have been extensively studied both experimentally and theoretically. Various phases can be obtained with interesting properties ranging from ionic superconductor A_3C_{60} (A = K, Rb, Cs) to isolating compounds K_4C_{60} and K_6C_{60} [1,2]. Fullerides with the significantly smaller alkali metals Li and Na are appealing because their behaviour deviates from that of compounds with heavier alkalis. The structural phase diagram of Na_xC_{60} shows stable phases with bulk stoichiometries of $x = 2, 4, 6$ [3–6]. For very low Na content, the valence band photoemission spectra present two structures near the Fermi level for which different assignments have been given in the literature. Wertheim et al. and Gu et al. [7,8] proposed that the two observed structures mirror a splitting of the t_{1u} band induced by the crystal field at the surface due to the reduced symmetry. De Seta et al. [9] modelled the spectra as a superposition of three different phases, namely C_{60}, Na_2C_{60} and Na_6C_{60}. In the low doping regime they found phase separation in C_{60} and Na_2C_{60}, where the latter gave rise to a spectral feature on the higher binding energy side. Schnadt et al. attributed the two features in their study of LiC_{60} [10] to a dimer phase (higher binding energy) and a rock salt phase (lower binding energy) similarly to what was found for A_xC_{60} with A = K, Rb, Cs [2].

Here we report a photoemission study of Na_xC_{60} which reveals, for the first time, an angular dependence of the valence band features. In the low doping range we also identify a metastable surface phase which disappears at higher doping.

2. Experimental

The experiments were carried out at the surface science end-station of beamline I-511 at MAX-lab [11]. The base pressure in the sample preparation chamber was 5×10^{-10} mbar. C_{60} films were prepared *in situ* by sublimation from a Ta crucible onto a clean Cu(1 1 1) surface. Na was deposited from well-degassed SAES getter sources. The crystal was heated resistively for the annealing cycles and its temperature measured by a thermocouple inserted in a hole on its side. Photoemission spectra were taken at normal and grazing (60°) emission.

The incidence angle of the synchrotron light was 8° grazing in both geometries. Valence band and Na 2p

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photoemission spectra were recorded with $h\nu = 110$ eV, the C 1s line with $h\nu = 354$ eV. The energy resolution was 80 meV (at 110 eV) and 100 meV (at 354 eV), respectively. The sample was at room temperature (RT) during data acquisition. All spectra were corrected for the transmission function of the photoelectron analyzer [12]. Since we observed small charging effects in the spectra which varied with emission geometry [13] the spectra presented here are shifted in order to align the shake up features of the C 1s line due to pristine C_{60}.

3. Results and discussions

3.1. Valence band spectra

In Fig. 1 valence photoemission spectra of samples with different amounts of Na are shown and compared to pristine C_{60}. Details on sample preparation are given in Table 1. In the following we focus on two aspects of the data, the development of new peaks in the LUMO-derived region and the changes in lineshape with photoelectron emission angle. As a general trend we observe that the width of the valence features is increased for Na-compounds (a – *h*) as compared to unreacted C_{60}. This suggests the existence of different phases as observed previously for Na-fullerides [14]. From their spectral shape and angular

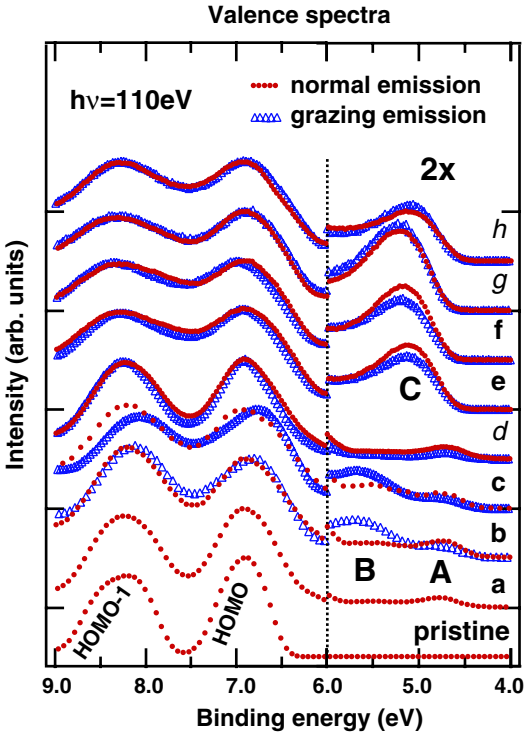

Fig. 1. PES of the Valence region. The normal emission spectra are aligned in energy to emphasize changes in lineshape. All spectra are normalized to the height of the HOMO-derived peak. The intensity of the LUMO-derived region is enlarged by a factor two. Solid lines indicate the position of peaks A, B and C. Increasing Na deposition (labels in bold) and heat treatments (labels in italic) are indicated in accordance to Table 1.

Table 1
Sequence of sample preparation steps

Sample	Preparation	T_S	Time
a	Na deposition	RT	16 min
b	Na deposition	RT	6 min
c	Na deposition	RT	6 min
d	*annealing*	420 K	225 min
e	Na deposition	360 K	23 min
f	Na deposition	360 K	6 min
Not shown	Na deposition	RT	16 min
g	*annealing*	520 K	20 min
Not shown	*annealing*	520 K	30 min
h	*annealing*	470 K	30 min

Each step consists of subsequent Na deposition and/or sample annealing. Deposition times and sample temperature T_S are given. Annealing steps are noted in italics.

dependence two groups of spectra can be defined. In the first group (a – *d*) two peaks A, B are observed in the LUMO-derived region. In the second group (e – *h*) there is only one peak C. Peaks A and B increase with Na exposure. After annealing of the sample to 420 K the intensity at A is reduced and feature B has disappeared. Both peaks are sensitive to the emission angle showing that there is a different electronic structure at the surface. None of the samples shows any spectral intensity at the Fermi level. Non metallicity agrees with Brouet et al. [15] who describe Na_2C_{60} as an insulator and with fact that no superconductivity has been found for Na_xC_{60} for $2 \leqslant x \leqslant 6$.

Let us now focus on the lineshapes at low doping. After the first deposition one peak, labeled A, is seen in the LUMO-derived region. Upon further Na deposition, peak B evolves and surpasses peak A in intensity (in the normal emission spectra). In the grazing emission spectra peak B is always more intense than peak A. Since Li and Na have a similar radius ionization potential and cohesive energy, we compare our data to the $Li_{x\leqslant 1}C_{60}$ result and tentatively assign peak B to a dimer phase (at higher binding energy) and peak A to a rock salt structure (at lower binding energy). Assignment for the latter is supported by the energy position of peak A with respect to the shoulder in the HOMO, which is like the HOMO–LUMO gap of 1.8 eV for pristine C_{60} [2]. However, structural investigations are needed to confirm this assignment. The angle dependence of the valence spectra in Fig. 1 indicates that feature B is present mainly at the surface. After annealing the sample to 420 K the intensity of both peaks A and B decreased (*d*). This observation suggests that either Na has diffused into the film or was lost during heating. We also note the relative intensity of feature B has significantly decreased after this annealing pointing to a metastable nature of the surface phase.

In order to achieve a higher Na concentration and a possibly a more homogeneous distribution of alkali ions in the sample, the crystal was kept at elevated temperatures during further Na exposure. The second group of spectra in Fig. 1 (e – *h*) refer to these samples and show a single peak C in the LUMO-derived region. The binding energy differ-

ence between peak C and the HOMO corresponds to the HOMO–LUMO gap of solid C_{60} [2]. We note that both the position and intensity of this peak depends very little on the exact stoichiometry in this doping range. Moreover, the valence spectra in this group show only a minor angle dependence and annealing at higher temperatures (520 K) for 20 min did not bring on spectral changes (*g*). From this we conclude that higher annealing and additional doping has induced structural changes of the composite, inducing a stable phase which is virtually the same in the bulk and at the surface.

3.2. Stoichiometry

To evaluate the sample stoichiometry we compared the area of the two highest occupied molecular orbital (HOMO and HOMO-1) with the area of the LUMO-derived peaks. Taking into account the number of electrons in the respective levels as well as the fact that there is an almost complete charge transfer for concentrations [16] $x \leqslant 6$, the stoichiometry can be deduced. The results are shown in Fig. 2. The difficulties in this determination arise because there is no clear separation between the frontier valence levels and the peaks in the LUMO-derived region. Hence we estimate the uncertainty of the values given in Fig. 2 with 15%.

For samples (b, c) there is a difference between the stoichiometry at the surface and in the bulk. Since there is no clear separation of surface and bulk signal in the higher valence peaks it is difficult to estimate the stoichiometry of the surface components. From our spectra it is likely that peak B is associated with a stoichiometry of $x = 1$. Peak A could correspond to a Na_2C_{60} phase, which is more stable in the anneal. After first annealing (*d*) the stoichiometry is reduced to only $x = 0.3$. The film has reached a more stable phase and a lower Na concentration. For the samples with Na exposure at elevated temperature we observe $x \approx 2$–3 and find only little variation with annealing temperature and additional Na deposition. For bulk samples with nominal stoichiometry Na_2C_{60} Klupp et al. [14] observe at RT phase segregation into C_{60} and Na_3C_{60}, and at high temperature a single phase Na_xC_{60}. The stoichiometry is different in the present case, due to different preparation steps and the presence of the surface layer, i.e., the number of available lattice places for C_{60} and Na is different.

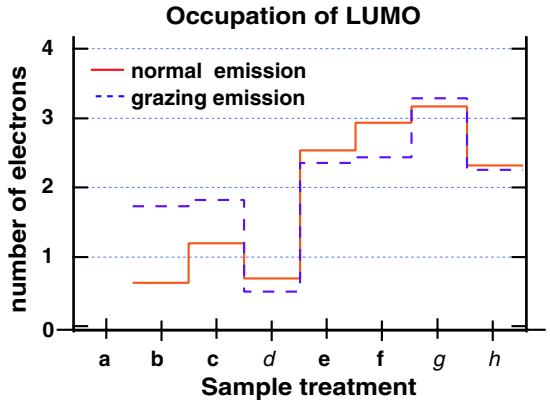

Fig. 2. Na_xC_{60} stoichiometry obtained from the ratio of the LUMO–HOMO and HOMO-1 area. See the text for more details.

3.3. C 1s spectra

In Fig. 3 C 1s core level photoemission spectra of the samples are displayed. To emphasize changes in lineshape, the spectra in the first group are shifted to line up with the shake-up structure of pristine C_{60}, in the second group spectra are shifted to align with the main peak position. The main line is asymmetric with a tail towards the low binding energy side. At grazing emission there is a slight shift of intensity towards higher binding energy, suggesting the existence of a surface component located at the lower binding energy side. In the second group the width of the C 1s line is increased and all spectra are virtually identical in normal and grazing emission. The lack of angular dependence in the second group shows that the chemical environment is similar at the surface and in the bulk. The variation

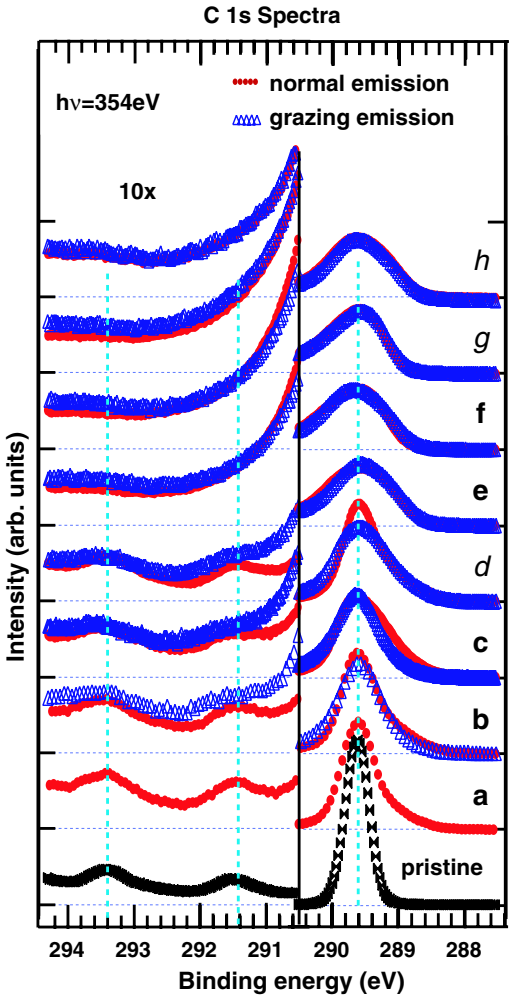

Fig. 3. PES of C 1s. The intensity of the shake-up region is enlarged by a factor ten. Increasing Na deposition (labels in bold) and heat treatments (labels in italic) are indicated. See text for more details.

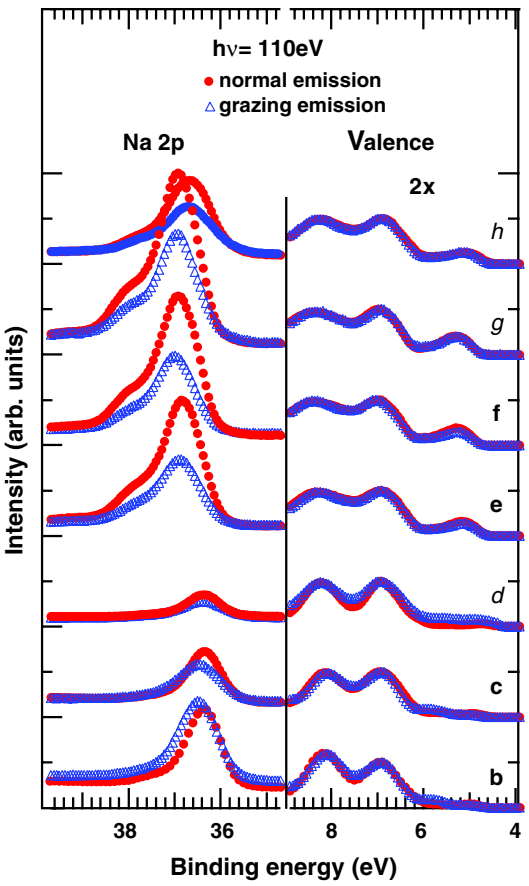

Fig. 4. PES of Na 2p. The spectra are aligned in energy to match the centroid of pristine C_{60} HOMO. See text for more details. Increasing Na deposition (labels in bold) and heat treatments (labels in italic) are indicated.

of the lineshape for the different samples shows that the C 1s line consists of different components, which we interpret as due to chemically different molecular sites.

3.4. Na 2p spectra

In Fig. 4 we show the Na 2p spectra scaled to normalize the intensity of the frontier valence region in order to compare relative intensities. In the first group the Na 2p peak is asymmetric and its lineshape changes little with emission angle. In the second group the peak is shifted towards higher binding energy and a shoulder on the high binding energy side is seen. Increasing Na intensity at normal emission is the evidence for a terminating layer of C_{60} in the second group. The ratio between shoulder and peak height is constant 2:1 in normal and grazing emission. From the 2:1 ratio in the double peak of the second group of samples we conclude that Na occupies tetrahedral and octahedral lattice sites, similar to K_3C_{60} [17,18].

4. Conclusions

The photoemission spectra of Na_xC_{60} thin films show for the low doping range two structures in the LUMO-derived band which we assign to a dimer phase for the feature at higher binding energy and to a rock salt structure at lower binding energy. We observe that the dimer phase is metastable, manifesting itself prevalently in the near surface region of the sample. Annealing produces a phase separation in pure C_{60} and rock salt. At higher doping the diffusion is sufficiently fast to equilibrate the sample at the annealing temperature. We find a stable phase $x \approx 3$ with a Na 2p lineshape characteristic for tetrahedral/octahedral occupation, similar to K_3C_{60}. No sign of metallicity has been found in the investigated samples.

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